Diffusion study of Electrodeposited Copper-Nickel Multilayer

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

Master of Technology (Dual Degree)

In

Metallurgical and Materials Engineering

Submitted By

Chinmaya Prasad Dakua

Roll No: 710MM1170

Department of

Metallurgical and Materials Engineering

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Under the guidance of

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CERTIFICATE

This is to certify that the thesis entitled, "**Diffusion study of Electrodeposited Copper-Nickel Multilayer**", submitted by **Chinmaya Prasad Dakua** in partial fulfillment of the requirements for the award of Master of Technology Degree in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela is an authentic work carried out by him under our supervision and guidance.

To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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Date: Chinmaya Prasad Dakua

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ABSTRACT

Copper and Nickel multilayer composites have been prepared by electro deposition of nickel on copper substrate from Watt's bath, producing Ni layer of low thickness and then subsequent deposition of copper on Ni by acidic sulfate bath, leading to electroplating of a thin Cu layer. Since adherent Nickel deposit cannot be deposited directly from conventional baths, copper substrate serves as an ideal undercoat for obtaining adherent Ni layer deposit with improved metal distribution and reduced critical cleaning & polishing requirements. Plating parameters such as current density and plating time are kept constant whereas the other bath compositions differ. This is done alternatively to generate alternate Cu-Ni metal multilayer. Magnetic stirring was applied during deposition process in order to produce homogeneous, smooth and adherent coatings of nickel. Characterization and surface morphology analysis is done using FESEM and optical imaging and thus, the thickness of the layers is obtained. The Cu-Ni multilayered composite is then subjected to vacuum heating so as to obtain the Time-Temperature profile and the extent of interlayer diffusion. This vacuum furnace heating was carried out in the presence of Argon gas, at different temperatures (773K, 973K, 1173K) and the samples are held at these temperatures each for different time intervals (1 hr, 2hrs, 3hrs). The resultant hardness, microstructure and the diffusion effects are then investigated and studied. The diffusion coefficients for Cu in Ni and Ni in Cu at the above mentioned temperatures was studied from theoretical calculation and subsequently compared with actual diffusion coefficients measured from the Energy Dispersive Spectroscopy (EDS) line scan.

Keywords: multilayer, interdiffusion, electrodeposition, diffusion coefficient, microhardness

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CHAPTER 1

Introduction

- Introduction
- Objectives and scope of the present study
- Scope of the thesis

1.1. Introduction

Multilayered alloy systems, in the recent past, have garnered a lot of attention from researchers since it has been explained that multilayer composites having sublayers of low thickness can exhibit better magnetic, electrical and mechanical properties than those that of the respective pure metals. These composites exhibit significantly higher Giant Magneto Resistance (GMR) effect and hence, have widespread applications in areas like interconnects, giant magneto resistive sensors, magneto-optical recording and data storage devices. It has also been observed enhanced tensile properties in electrochemically produced Cu-Ni multilayer films. Also morphological study of transition metal-based thin films is of great importance for acquiring unique physical and chemical properties, for example, carbon nanotubes.

Electrodeposition technique to develop alternate layers of metals on a conductive substrate surface in a multilayer alloy system is quite widely used and the properties of the multilayer deposits are significantly affected by parameters such as the electrolyte concentration, Ph and the deposit potential, additive substrates and the control methods (potentiostatic and galvanostatic). The Watts solution is one of the most common techniques for electroplating nickel on the material substrate, but Watt's bath produces stresses to the plated material which leads to lower fatigue properties. Ultrasonic agitation during deposition is required to lower the stress limit of the plating material along with increased current efficiency and current density of the plating bath which in turn decreases the coating time. Sulphate or acidic bath for depositing copper is a popular method with current density and Ph of the electrolyte remaining constant during the entire plating process.

Diffusion of the Cu-Ni multilayer system is important from the point of view of its application in microelectronics industry. Nickel acts as a suitable diffusion barrier for copper. Vacuum heating of the multilayer system is essential in the presence of an inert gas such as argon since oxidation of the alloy system may occur in the usual heating system, when the composite is heated at an elevated temperature (but not below the melting temperature of both metals) for extended periods of time.

1.2. Objectives and scope of the present study

The present work aims at diffusion study of electrodeposited Cu-Ni multilayer alloy carried out at different time and temperature. Detailed objectives and work flow of the research work are briefly listed below:

1. Electrodeposition of nickel layer on copper foil substrate from Watts bath and then subsequent deposition of copper layer from sulphate bath in order to produce Cu-Ni multilayer composite. The plating parameters such as current density and plating time are kept constant during the plating process.
2. Characterizations
   - Microstructure and morphology (Optical imaging, SEM, FESEM)
   - Surface mechanical properties (Hardness)
3. Vacuum heating of the electrodeposited Cu-Ni multilayer alloy in the presence of argon gas at different temperatures (773K, 973K and 1173K), each for different time periods (1 hr, 2 hrs and 3 hrs), so as to study the diffusion properties.
4. Characterizations of the heated samples
   - Microstructure and morphology (Optical imaging, SEM, FESEM)
   - Chemical analysis (EDS)
   - Surface mechanical properties (Hardness)
5. Comparative study between the theoretical diffusion properties and the observed diffusion properties with the help of EDS line scan.

1.3. Scope of the thesis

The organization of the rest of the theses is described. The concept of multilayered alloys, surface engineering, electrodeposition technique, electroplating of Ni, electroplating of Cu, diffusion mechanism, brief review of literatures on electrodeposited Cu-Ni multilayer and its inter-diffusion properties has been presented in chapter 2. The experimental procedure such as sample preparation, electrodeposition methodology, optical imaging & FESEM analysis and micro hardness testing process has been depicted in chapter 3. Chapter 4 describes the characterization & hardness results and EDS line scan analysis of the heated samples. Chapter 5 provides a summary of the main findings of the study along with the conclusions drawn. Chapter 6 provides the references.

CHAPTER 2

Literature Review

- **Multilayered alloys**
- **Surface engineering**
- **Electro deposition**
- **Electroplating of copper**
- **Electroplating of nickel**
- **Brief review of the literatures on Cu-Ni multilayer system**
- **Diffusion**
- **Brief review of the literatures on inter-diffusion in Cu-Ni system**

2. LITERATURE REVIEW

2.1. Multilayered alloys

Multilayered alloys are metallic composite structures, comprising of alternating layers of two different metals, periodically deposited on a pure metal substrate or alloy substrate, by electrodeposition or vacuum deposition techniques. The electrodeposition of multilayers has been reviewed [1]. In the recent years, there has been an overwhelming interest in the study of metallic multilayers [1, 2] owing to the fact that these multilayers exhibit enhanced magnetic, electrical, diffusion and mechanical properties as compared to the those that of the corresponding pure metals. It has also been demonstrated [2, 3] that electrodeposited multilayer can also exhibit a giant magneto resistance (GMR) effect.

Electrodeposited multilayers can have a structural quality comparable to those of the multilayers grown by vacuum techniques [4]. X-ray diffraction (XRD) showed that some electrodeposited multilayers can exhibit satellite peaks up to the fifth order [5] in the high-angle region and Bragg peaks up to the sixth order [6] in the low-angle region.

Though the diffusion characteristics of the thin Cu-Ni multilayers have already been extensively studied [7, 8], but there have been very few studies regarding the intermixing during deposition. The properties of the multilayer deposits are significantly affected by parameters such as the electrolyte concentration, Ph and the deposit potential, additive substrates and the control methods (potentiostatic and galvanostatic). The effect of these parameters has been studied extensively [9, 10].

2.2. Surface Engineering

Surface engineering involves the complete field of research and technical work utilized for the production, design and investigation of surface layers for properties better than the core.

These techniques can be used to produce a great range of functional properties at the required substrate surfaces, including chemical, mechanical, electrical, magnetic, corrosion-resistant and wear-resistant properties [11].

2.2.1. Techniques of Surface Modification

- Electroplating- Electroplating, otherwise known as electrodeposition, is a method of coating in which the anode, made of the depositing material, is dipped into an electrolyte bath containing the cathode, which is the substrate on which deposition needs to take place, and the metal ions travel through the solution and get deposited on the cathode substrate surface on application of electric current.
- Electro-less plating- In this process, the metal ions from the electrolyte get deposited on the cathode substrate surface as a result of chemical reactions occurring on the substrate surface. Here, no electric current is involved.
- Conversion coating- In this process, non-metals get deposited on the metal surface as compounds of the substrate metals as a result of chemical or electrochemical reactions on the metal surface.
- Hot dipping- In this process, the metal substrate is dipped into a molten metal bath, forming a layer of metal on the substrate surface after removal of the substrate from the molten bath.

- Physical Vapour Deposition (PVD) - In this technique, the material to be deposited is first vaporized in vacuum, then transported to the substrate and then condensation of the vapour on the substrate surface takes place.
- Chemical Vapour Deposition (CVD)- This is the process, in which the coating is formed on the hot substrate surface placed in an atmosphere of a mixture of gases, as a result of chemical reaction or decomposition of the gases on the substrate material.
- Thermal spraying- It is a process of deposition of the atomized metal at elevated temperature by its delivery at the metal substrate surface through high velocity gas stream.

2.2.2. Methods of production of metallic multilayer

Though there are various techniques for altering the metal substrate surface or depositing a layer of similar or dissimilar material on the substrate [1, 3], however, the commonly used methods for production of metallic multilayered composites are as follows:

- Molecular beam epitaxy- Molecular beam epitaxy is a PVD technique that takes place in high vacuum or ultra-high vacuum (10^{-8} Pa). The most important aspect of MBE is the deposition rate (typically less than 3000 nm per hour) allowing the films to grow in an epitaxial manner.
- DC magnetron sputter deposition- Magnetron Sputtering is a Plasma Vapor Deposition (PVD) process in which a plasma containing argon ions and electrons is generated first, followed by ejection of atoms from the target after being stuck by the argon ions, and then final deposition of the atoms on the substrate after travelling through the plasma. It can be used to coat films as thin as 1 or 2 nm.

- Ultra high vacuum evaporation- In this PVD technique, the material to be deposited is first heated to a gas phase where it then diffuses through an ultra-high vacuum to the substrate.
- Electrodeposition- Also known as electroplating, it is the most commonly used method for developing metallic multilayered composites.

However, the multilayers produced by electrochemical technique have been found to be of improved and better quality than those produced by other physical routes [12].

2.3. Electrodeposition

Electro deposition is the process of coating a thin layer of one metal on top of a different metal to modify its surface properties. Also known as electroplating, it involves the reduction of cations of the desired material from the electrolyte on application of electric current and subsequent deposition of the cations on the conductive metal substrate surface. It is done to achieve the desired electrical and corrosion resistance, reduce wear & friction, improve heat tolerance and for decoration. Electrodeposition is a surface coating method that forms an adherent layer of one metal on another. It can be used to develop variety of bulk products ranging from macro to nano scale. Since coating is to be ensured, the material substrate is itself taken as cathode.

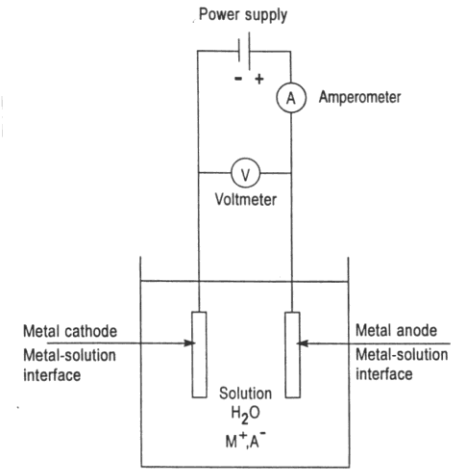


Figure 2.1. Electroplating experimental setup for deposition

of metal M on cathode substrate [13]

Figure 2.1 demonstrates an experimental setup for electrodeposition of a metal M upon application of required potential or current density, the metal ion M+ are deposited on cathode substrate after travelling through the previously prepared electrolyte bath or solution.

2.3.1. Requisites for electroplating

The following factors are to be essentially considered before and during the electrodeposition process:

- Conducting surface as a seed layer is needed.
- Clean containers, substrates and solutions are required since even low impurity levels can lead to poor quality films.
- Uniform current distribution on the substrate surface is essential for uniform adhesion of coating.
- Good resist adhesion on the substrate is important.

- The plating solution must be compatible with the substrate and resist materials.

2.3.2. Factors on which electroplating depends

The morphology and the composition of the electrodeposits differ substantially and depend upon the following factors:

- Current density
- Bath composition and temperature
- Solution concentration
- Presence of impurity
- Nature of anions and cations in the solution
- Physical and chemical nature of the substrate surface
- Type of power supply waveform and Ph

2.3.3. Advantages of electrodeposition

- It is inexpensive and industrially applicable as it involves little modification in existing electroplating technology for deposition.
- It can be up scaled with relative ease for use in large sized parts.
- The experimental setup used is much simpler.
- Most importantly, it is a room temperature technology and beneficial for systems in which undesirable inter-diffusion occurs between the adjacent layers during deposition.

2.3.4. Methods of production of electrodeposited multilayer

Now there are two methods for producing electrodeposited alternated layers of two different metals, the single-bath method [12,13] the dual-bath method [14]. In the dual-

bath method, two different baths (one for each metal) are alternatively used whereas, in single-bath method, two metallic ions are present in the same electrolyte.

2.4. Electroplating of Copper

Coatings of copper may be deposited very readily by electroplating. The baths that are commonly in use are sulphate, cyanide and pyrophosphate bath. Other baths that are rarely used for plating are the fluoborate bath, sulphomate bath and alkaline sulphomate bath.

However, the most widely used bath for copper deposition is the sulphate bath or the acidic bath.

2.4.1. Sulphate bath

The sulphate bath composition includes copper sulphate (200g/l), sulphuric acid (50 g/l) and the plating parameters include current density of 5 A/dm2 and plating potential of 0.6V with 95% current efficiency. The metal substrate is taken as cathode and copper electrodes is taken as anode and on application of the essential electric current, copper ions migrate through the bath and gets deposited on the metal substrate.

2.4.2. Advantages of adding H_2SO_4 to the bath

- Increases conductivity of the bath.
- Increases the throwing power of the solution.
- In absence of sulphuric acid, there is formation of basic copper salts during electrolysis which interfere with electrolysis and deposition process.

2.4.3. Process

The reactions involved during the process are as follows:

$CuSO_4 = Cu^{2+} + SO4^{2-}$

$SO_4^{2-} + H_2O = H_2SO_4 + O$ (At anode)

$Cu^{2+} + 2e = Cu$ (At cathode)

Thus there is constant increase in the sulphuric acid content due to which anode dissolution is effected to some extent. More copper goes into solution. Copper removed in the bath shall be replaced by anode. The concentration of the copper ion in the bath is constant. Figure 2.2 depicts the experimental setup for copper plating on cathode metal Me, with copper metal Cu acting as the anode.

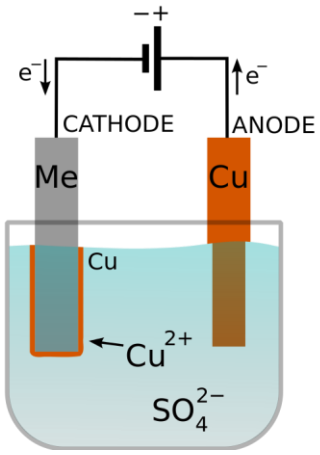


Figure 2.2. Experimental setup for copper electroplating

on cathode metal Me, Cu acting as anode

2.4.4. Applications of copper deposits

- As an undercoat for other metal coatings- Copper plating is used as an undercoat prior to Ni/Cr plating on steel, zinc base die castings, and aluminium steel. There are three advantages of using copper plating as an undercoat:
  - Polishing coat is reduced.
  - Metal distribution is improved.
  - Less critical cleaning for achieving a well adherent Ni deposit is required.
- As a decorative finish on Zinc base alloys or steel.
- Providing conducting surfaces on non-metallic materials.

2.5. Electroplating of nickel

The various electrolyte baths commonly are the Watts solution, all chloride solution and bright nickel solutions [15]. Few other baths are sulphamate solution, black nickel plating and all sulphate solution fluoborate solutions.

However, the most widely used electrolyte bath for nickel plating is the Watts bath.

2.5.1. The Watts Solution

It is the most popular nickel electroplating solution. Plating operation in Watts solutions is low cost and simple. The substrate to be plated is used as cathode, i.e. negatively charged to the DC supply and a nickel plate is used as anode.

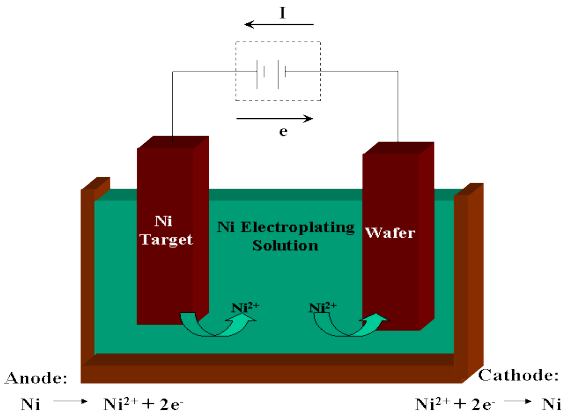


Figure 2.3.Ni electroplating on wafer substrate with Ni target

acting as anode with a suitable electrolyte solution

Figure 2.3 depicts the nickel deposition experimental setup wherein the nickel target acts as the anode metal and deposition of nickel takes place on wafer cathode substrate. The bath composition for the Watts bath include nickel sulphate decahydrate (350g/l), nickel chloride decahydrate (45g/l) and boric acid (37g/l) with the plating parameters being 5A/dm^2 current density and constant temperature in the range of 55-65^{o}C.

2.5.2. Role of different constituents in the bath

- NiSO4: This is major source of nickel ion. It is cheaper salt of nickel having a stable anion.
- NiCl2: It is added for the following purposes-
  - To overcome the passivity of the anode.
  - To assist in uniform anodic dissolutions.
  - To improve the conductivity.
  - To enhance the cathode efficiency.
- Boric acid: It is the buffer agent and buffers at about Ph 9 or 5 (maintaining the acidity of the solution and preventing vide fluctuations of the Ph or concentration of hydrogen ions). The addition of boric acid makes the deposit white and refines the gran due to buffering action.
- Anodes: Pure nickel anodes suffer passivity. Hence, the anodes are contaminated with impurity. Following are the two types of anodes used-
  - Contaminated with Fe-C (Ni-92%, Fe-3%, rest C)
  - Contaminated with S (S-0.005 to 0.05%, rest Ni)

2.6. Brief review of the literatures on electrodeposited Cu-Ni multilayer system

N. Rajasekaran et al. [16] used potentiostatic electrodeposition to produce Cu–Ni multilayer by two-wave pulse plating technique from sulphate/citrate electrolyte at pH 4. Adherent, smooth and bright deposits of Cu–Ni multilayer coatings were two-wave pulse plated successfully on copper substrates. Uniform coverage with spherical nodular morphology and smoothness of these coatings is observed from microstructure analysis. The Cu–Ni multilayer deposits, obtained from bath composition and bath parameters are mentioned and demonstrated excellent corrosion protective performance.

Ch. Bonhote et al. [17] electrodeposited Ni-Cu multilayers of sublayer thickness 20 nm and 10 nm respectively from a citrate electrolyte and demonstrated that during electrodeposition of nickel copper multilayers from a citrate electrolyte the microstructure of the deposit can be controlled independently of the thickness of the sublayers. The latter depends on the charge passed during a given cycle while the former depends on the value of the applied current density for copper deposition with respect to the limiting current density.

Surendra Singh et al. [18] conducted a detailed study of Cu-Ni multilayer films produced by electrodeposition technique and concluded that Electrodeposited film shows a granular growth of film with a distinct quasi-two-level surface morphology. The DNS data reveals the detailed morphology of buried interfaces. The interfaces grown by sputtering technique show a self-affine rough fractal surfaces with a small correlation length of _400A˚, whereas the Cu/Ni and Ni/air interface (grown by ED method) are found to be almost two-dimensional with a rather large

correlation length of _ 1300A˚ , which is in the same range as the island size in lateral dimension.

Alper et al. [19] electrodeposited Ni–Cu/Cu multilayers on (1 0 0) textured polycrystalline Cu substrates from an electrolyte with different pH values. It has been demonstrated that the multilayers have different growth modes for different electrolyte pH values and have the same crystal structure (fcc) and (1 0 0) texture as their substrates. It was found that the Cu content of magnetic layers increases with increasing electrolyte pH. The multilayers grown at high electrolyte pH (3.0) have rougher surfaces compared to those at low electrolyte pH (2.0). The GMR behavior was found to be similar to that of granular type alloys in which the magnetic regions exhibit superparamagnetism.

2.7. Diffusion

Diffusion is a mass flow process by which atoms (or molecules) change their positions relative to their neighboring particles under the influence of thermal energy and a gradient.

This mass transport phenomenon can be depicted by the use of a diffusion couple, for example Cu-Ni diffusion couple, when it is heated for an extended period at an elevated temperature (but below the melting point of both metals), and cooled to room temperature.

Figure 2.4.Copper-nickel diffusion couple before high temperature heat treatment

Copper and nickel remain at the two extremities of the couple separated by an alloyed region as shown in the figure 2.5. Concentrations of both metals vary with position as shown in Figure 2.6.

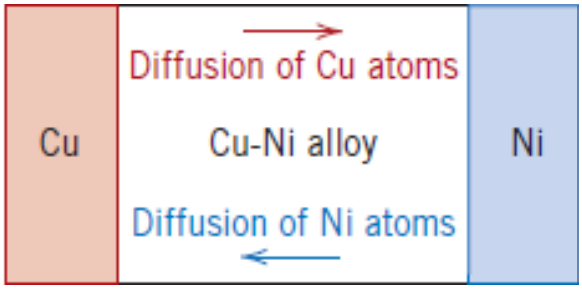


Figure 2.5.Copper and nickel after the heat treatment separated by an alloyed diffusion region

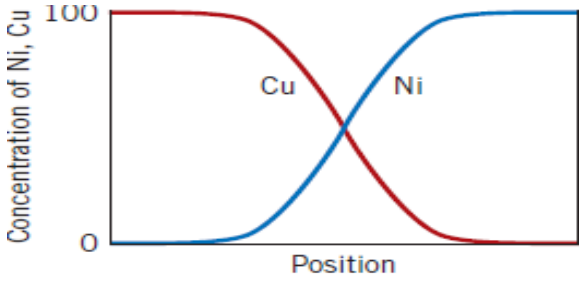


Figure 2.6.Variation of Cu and Ni concentrations with position x across the couple

This result indicates that copper atoms have diffused into the nickel, and that nickel has diffused into copper. This process, whereby atoms of one metal diffuse into another, is termed interdiffusion, or impurity diffusion. Interdiffusion may be discerned from a macroscopic perspective by changes in concentration which occur over time, as in the example for the Cu–Ni diffusion couple. There is a net drift or transport of atoms from high- to low-concentration regions. Diffusion also occurs for pure metals, but all atoms exchanging positions are of the same type; this is termed self-diffusion.

2.7.1. Diffusion Mechanisms

Diffusion is the migration of solid atoms from one lattice site to another and for an atom to accomplish such migration, two conditions must be met: (1) there must be an empty adjacent site, and (2) the atom must have sufficient energy to break bonds with its neighbor atoms and then cause some lattice distortion during the displacement. This energy is vibrational in nature. The two most dominating mechanisms of diffusion are discussed below:

- Vacancy diffusion: It involves the interchange of an atom from a normal lattice position to an adjacent vacant lattice site or vacancy. Since diffusing atoms and vacancies exchange positions, the diffusion of atoms in one direction corresponds to the motion of vacancies in the opposite direction. Both self-diffusion and interdiffusion occur by this mechanism; for the latter, the impurity atoms must substitute for host atoms.
- Interstitial diffusion: It involves atoms that migrate from an interstitial position to a neighboring one that is empty. This mechanism is found for interdiffusion of impurities such as hydrogen, carbon, nitrogen, and oxygen, which have atoms that are small enough to fit into the interstitial positions.

In most metal alloys, interstitial diffusion occurs much more rapidly than diffusion by the vacancy mode, since the interstitial atoms are smaller and thus more mobile. Also, there are more empty interstitial positions than vacancies; hence, the probability of interstitial atomic movement is greater than for vacancy diffusion.

2.7.2. Steady-state diffusion

Diffusion is a time-dependent process. The rate of diffusion or the rate of mass transfer is expressed as diffusion flux (J), defined as the mass M diffusing through and perpendicular to a unit cross-sectional area of solid per unit time. In mathematical form,

$$J = \frac{M}{At}$$

Where A is the area across which diffusion is occurring and t is the elapsed diffusion time. The unit for J is kg/m2s or atoms/m2s.

The driving force for diffusion in steady-state is the concentration gradient and mathematically, diffusion flux is proportional to the concentration gradient, given as:

$$J = -D\frac{dC}{dx}$$

Where D is the diffusion coefficient expressed in square meters per second and the negative sign indicates the direction of flow from high concentration to low concentration.

The above equation is also termed as Fick's first law for diffusion. One practical example is the purification of hydrogen gas.

2.7.3. Non steady-state diffusion

Diffusion in most cases varies with the time of diffusion. Under conditions of non-steady state diffusion, Fick's second law persists, given as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

If the diffusion coefficient is independent of composition, this equation simplifies to:

$$\frac{\partial C}{\partial t} = D\frac{\partial 2c}{\partial x2}$$

Figure 2.7 shows the concentration profiles for non-steady state diffusion at three different time t1, t2 and t3.

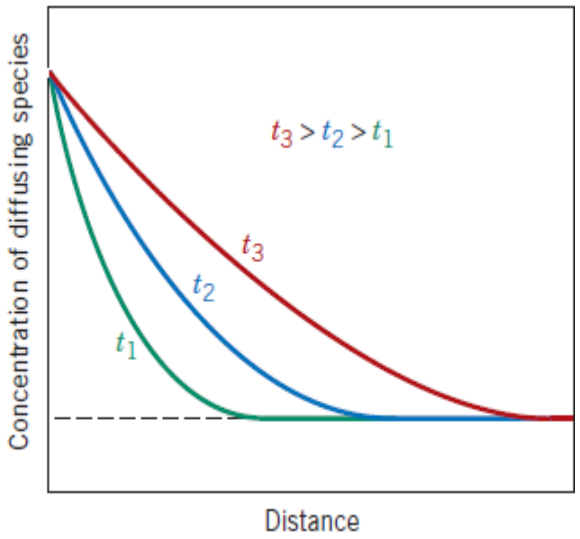


Figure 2.7. Concentration profiles for non steady state diffusion a times

t1, t2 and t3

One practical solution to the Fick's second equation can be determined after suitable assumptions taken for a semi-infinite solid with a constant surface concentration, in which the diffusing species is a gas phase maintained at a constant pressure values, such as the following:

- Before diffusion, any of the diffusing solute atoms in the solid are uniformly distributed with the concentration of C0.
- The value of *x* at the surface is zero and increases with distance into the solid.
- The time is taken to be zero the instant before the diffusion process begins.

Furthermore, applying the required boundary conditions, the following solution is yielded:

$$\frac{Cx-C0}{Cs-C0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

or,
$$C(x,t) = 1 - erf\,\frac{x}{2\sqrt{Dt}})$$

Also, to compute the concentration of a particular species in another, sometimes the following relationship is used for calculation:

$$\frac{x2}{Dt} = constant$$

2.7.4. Factors that influence diffusion

The factors which dominantly influence the rates of diffusion are as follows:

- Diffusing species- The magnitude of the diffusion coefficient *D* is indicative of the rate at which atoms diffuse. The diffusing species as well as the host material influence the diffusion coefficient. For example, there is a significant difference in magnitude between self-diffusion and carbon interdiffusion in iron at 500 C, the *D* value being greater for the carbon interdiffusion. This comparison also provides a contrast between rates of diffusion via vacancy and interstitial modes. Self-diffusion occurs by a vacancy mechanism, whereas carbon diffusion in iron is interstitial.
- Temperature- Temperature has a most profound influence on the coefficients and diffusion rates. For example, for the self-diffusion of Fe in -Fe, the diffusion coefficient increases approximately six orders of magnitude rising temperature from 773K to 1173K. The temperature dependence of diffusion coefficients is given as:

$$\text{D} = \text{D}_0\text{exp}\left(-\frac{Q}{RT}\right)$$

Where, D0 = a temperature-independent preexponential (m2/s)

R = Universal gas constant (8.31 J/mol-K)

T = Absolute temperature (K)

Q = Activation energy for diffusion (J/mol or ev/atom)

The activation energy is the energy required to cause the motion of one mole of diffusing atoms. Higher the activation energy, lower is the diffusion coefficient for the species.

2.8. Brief review of the literatures on interdiffusion in Cu-Ni multilayer system

The importance of understanding diffusion processes in thin films for controlling the quality of microelectronic devices, in terms of both efficiency and stability, does not need to be emphasized. The degree of interdiffusion in copper–nickel thin films is of considerable interest in the microelectronics industry, so it has been extensively investigated [20], and it is still a subject of current researches [21, 22] using a variety of analytical models and techniques. The poor adhesion of copper with some kinds of substrates in chip-packaging devices could be a problem. Therefore, an intermediate metal such as nickel is deposited first to reduce the diffusion and to improve the adhesion between copper and its substrate [23]. Nickel is efficient to be used as a diffusion barrier for copper in microelectronic devices, especially in solder applications [24].

Lefakis et al. [20] explained that copper is a fast diffuser into silicon substrate and this could deteriorate the p–n junction since copper is widely used in microelectronics and silicon solar cells.

Abdul-Letiff et al. [21] explained that the diffusion parameters of thin film systems are strongly affected by the film microstructure and by the heat-treatment ambient. Grain boundaries and other kinds of crystal defects play a dominant role in the diffusion process. Interdiffusion in the investigated copper–nickel thin films can be described by type B Kinetics in which rapid grain boundary diffusion is coupled to defect-enhanced diffusion into the grain interior.

Divinski et al. [22] reported on GB diffusion of Ni in high-purity polycrystalline Cu. The activation enthalpy of Ni diffusion in Cu general high-angle GBs is HNi gb ¼ 90:4 kJ mol_1, which is larger than the activation enthalpy of Cu GB self-diffusion (HCu gb ¼ 72 kJ mol_1). The absolute values of Ni GB diffusivity were significantly (by two orders of magnitude) smaller than the GB self-diffusion of Cu in the temperature range of the present C-type measurements. This difference was attributed to probable Ni segregation to sub-interface sites. The larger value of Ni surface tension in comparison to that of Cu forces Ni to occupy sub-interface sites and slows down the Ni GB diffusivity.

Ahmed M. Abdul Letiff [23] explained that a significant diffusion of Ni through Cu layer exceeding 12 at% level occurred upon annealing at 5001C for 5 min, at 4001C for 20 min, at 3001C for 80 min, and at 2001C for 180 min and concluded that the measured Ni concentration profiles represent the composite result of a small contribution by rapid grain-boundary diffusion followed by a large contribution of defect assisted diffusion into the grain interior.

Meunier et al.[24] had studied the Ni/Cu(0 0 1) epitaxied system using AES and found that a dynamical segregation of Cu atoms occurred during the MBE growth of Ni.

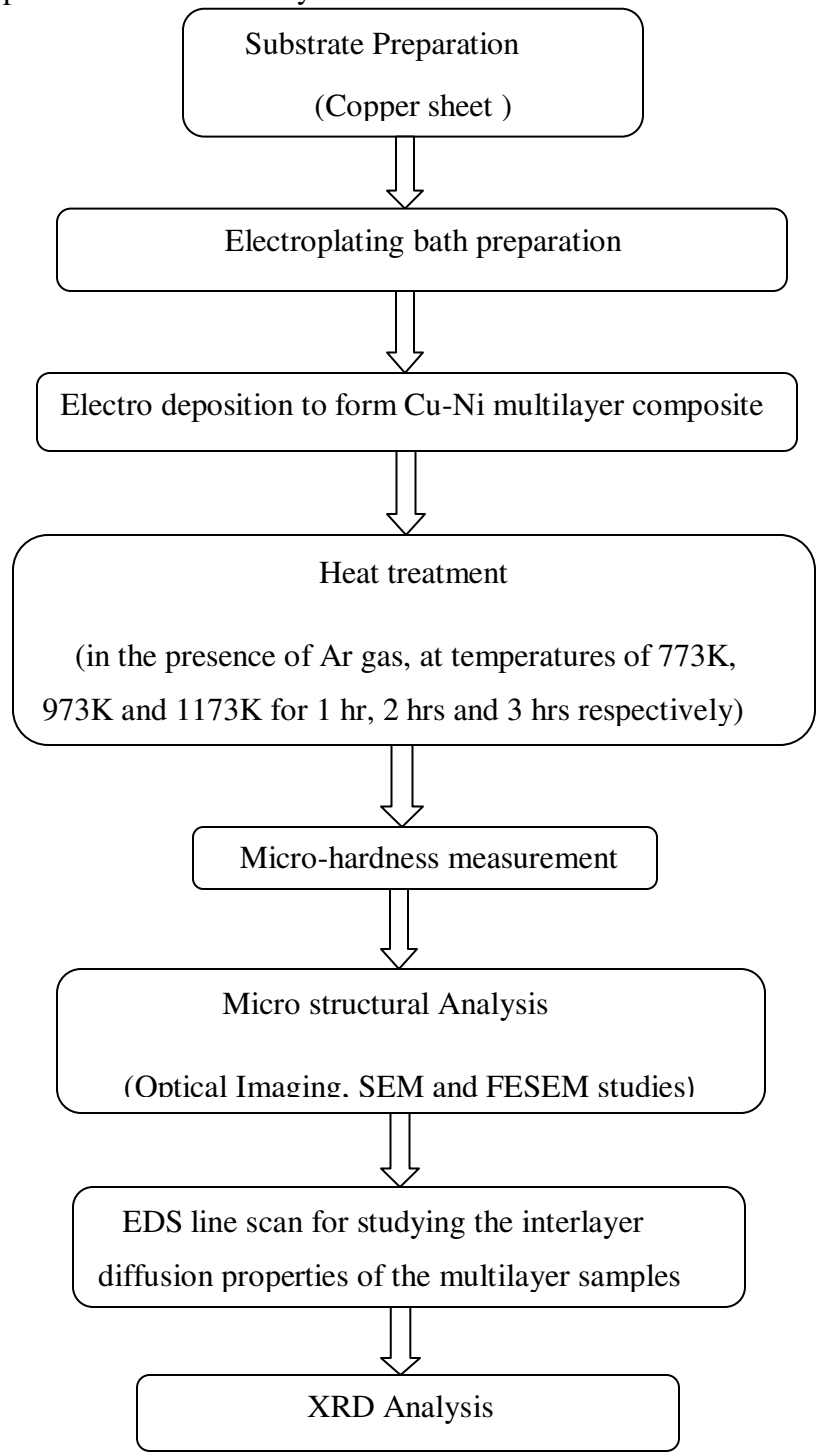
CHAPTER 3

Experimental Procedure

- Experimental flowchart
- Substrate and sample preparation
- Electroplating bath preparation
- Vacuum heat treatment
- Micro structural characterization
- Chemical analysis (EDS)
- Micro hardness measurement
- XRD analysis

3.1. Experimental Flowchart

The flowchart below depicts the methodology that had been adopted during the entire process of experimentation and study.



3.2. Substrate and specimen preparation

Copper specimens with approximate dimensions of 23mm x 13mm x 3mm were taken as the substrate for electro deposition. For attaching the samples in the electroplating system, holes were made in the samples. Initially, the copper foil substrates were metallographically polished using emery grade papers (1/0, 2/0, 3/0 and 4/0) and moving belt polisher. Then they were cleaned and degreased with acetone in order to eliminate the impurities without any activation pre-treatment. The base of the copper substrate was covered with non-reacting coat, such as nail polish, so that deposition does not occur at the base and plating of nickel and copper takes place only on the required substrate surface.

After the electroplating procedure for obtaining Cu-Ni samples, the samples were subjected to vacuum heating after being cut into equal parts in a vertical direction and the cross-sectional portion of each sample after heating was hot mounted using copper powder, polished again using emery grade papers, moving belt polisher, cloth polisher using alumina and diamond polished eventually.

3.3. Electroplating bath preparation

The Cu-Ni multilayer alloy system was prepared using electrodeposition of nickel on the copper foil substrate from Watts bath so as to obtain nickel layer of low thickness and subsequent deposition of copper on the already plated nickel layer using acidic bath so as to obtain copper layer of appropriate thickness.

3.3.1. Watts bath for plating nickel

Electro deposition of Nickel on the copper substrate was done using the Watts solution. The composition of the bath along with the plating parameters are shown below in Table. Prior magnetic stirring was done before and during the plating process so as to maintain the required temperature. The temperature was maintained by using hot plate and the electro deposition was controlled by DC source. The prepared copper substrate was used as cathode whereas a nickel plate, contaminated with Fe-C, was used as anode. The Ph of the plating solution was maintained by adding ammonium hydroxide(for increasing ph) and acetic acid(for decreasing ph), between 3-4.

Table 3.1: Watts bath composition and plating parameters

Electrolyte (Watts bath)	Nickel sulfate ($NiSO_4.6H_2O$): 350 g/l Nickel Chloride ($NiCl_2.6H_2O$): 45 g/l Boric acid (H_3BO_3): 37 g/l
Ph	~4
Temperature	55-65^oC
Current density	5A/dm2
Plating time	40 min

A potential of approximately 2.5V was set to produce the required current density for electroplating of nickel on each Cu substrate as the current density needed to be kept constant. After that, the layer of Ni was washed carefully and dried using hot-air blowing. The plating time of 40 minutes was kept constant also.

3.3.2. Sulphate bath for electroplating copper

Then, for subsequent electro deposition of copper layer on the previously deposited adherent, distinct and continuous nickel layer, sulphate bath or acidic bath was utilized. The composition of the bath along with the plating parameters are shown below in Table 2.

Table 3.2: Acidic bath composition and plating parameters

Electrolyte	Copper sulphate ($CuSO_4$): 200 g/l Sulphuric acid (H_2SO_4): 50 g/l
Current density	5A/dm^2
Current efficiency	95%
Plating potential	0.6V
Plating time	40 min

For this, the previously prepared Cu-Ni deposit was taken as cathode and a copper plate was taken as anode. A potential of 0.6V was applied through the DC source to produce the required current density for electroplating since the current density needed to be kept constant. The plating time in this case too, was kept constant, i.e. 40 minutes.

Sulfuric acid increases the conductivity of the bath and in its absence; there are chances of formation of basic Cu salts during electrolysis that interfere with electrolysis and subsequent deposition. As a result, a fine grained Cu deposit is obtained on the Ni sub layer with low thickness in the range of micrometers.

3.4. Heat treatment

The electrochemically produced Cu-Ni multilayer samples were then subjected to heat treatment. These samples were vacuum heated using the Honeywell programmed OKAY Electric furnace with model number 3104C-580, in the presence of Argon gas, at different temperatures (773K, 973K and 1173K) each held for different periods of time (1 hr, 2 hrs and 3 hrs) respectively. Care was taken to maintain the optimum pressure during annealing process such that no oxidation takes place.

3.5. Microstructural characterization

3.5.1. Optical microscope studies

The cross-sectional surface morphology of the electrodeposited Cu-Ni multilayer, before and after the heat treatment procedure, was obtained by using optical microscope by ZEISS with model number 3327000403. The Cu-Ni compositionally modulated multilayer obtained by electro deposition, now that is subjected to optical imaging, AXIO vision Release 4.8 software was used to determine the nickel and copper sublayers at the cross-section, and obtain the thickness of the multilayer for its use in analyzing the diffusion properties of the composite.

3.5.2. SEM and FESEM studies

Scanning Electron Microscope (SEM) gives morphology and composition of samples which is obtained by JEOL instrument with model number JSM-6480 LV scanning electron microscope (SEM) fitted with an energy dispersive X-ray detector of Oxford data reference system. The collection area and the number of electrons collected decide the pixels

given in terms of resolution. The depth of penetration of the electrons depends on the conductive nature of the sample. Hence the surface features can be analyzed by Secondary electron mode.

The prepared samples were subjected to gun-assisted Field Emission Scanning Electron Microscope (FESEM). Characterization in NOVA NANOSEM 450/FEI was done to obtain clear image of the Cu-Ni sub layers at the cross-section with better resolution of the micrographs.

3.6. Chemical analysis (EDS line scan)

The heat treated Cu-Ni samples were subjected to FESEM analysis, wherein the Energy Dispersive Spectroscopy (EDS) line scan for each sample was done so as to demonstrate the diffusion at the Cu-Ni interface. This scanning using EDS by Brooker, Germany; for diffusion rate for copper and nickel versus the depth of the sub layers in the samples, helping compare the observed diffusion effects with the theoretical diffusion characteristics.

3.7. Micro hardness measurement

Micro hardness measurements were carried out on the surfaces of Cu-Ni multilayer samples, both before heating immediately after electroplating and then after the heat treatment process of each sample. Tests were conducted using a Vickers micro hardness tester (LECO) with 25 g load. Each hardness value reported here is an average of 4-5 measurements on the same sample at equivalent locations.

3.8. Calculation of diffusion parameters

The diffusion profile from EDS line scan was studied for each sample, heated at different temperatures 773K, 973K and 1173K at different time intervals 1 hr, 2 hrs and 3 hrs, by calculating the diffusion depth x for copper in nickel layer at a particular time t for a certain temperature T and then we used the governing equation:

$$\frac{x2}{Dt} = constant$$

Or, $x^2 = Kt$

Where K is a constant for each temperature T and is proportional to D.

The K values for each temperature at different time periods were found out by finding the slope of the graph plotted between x2 versus t.

K_{500}, K_{700} and K_{900} values were obtained from the slope of the respective x^2 vs t plots.

Then, using the Arrhenius equation:

$$K = K_0 \exp\left(-\frac{Q}{RT}\right)$$

Or, $$\ln K = \ln K_0 - \frac{Q}{RT}$$

And plotting a graph between lnK and 1/T and comparing this with the equation for straight line:

$$Y = mX + C$$

We obtained Q and K_0 values with K_0 being the intercept and –Q/R being the slope of the graph. Since K_0 is proportional with D_0 values and hence comparing the values obtained with the theoretical values, we established an analytical and comparative study between the theoretical and observed diffusion values for diffusion of copper in nickel.

Thus, a comparative study was established for the diffusion parameters in the case of diffusion of copper in nickel sub layer.

3.9. XRD analysis

To study the effect of crystalline grain size of copper on the diffusion of Cu in Ni, XRD analysis of copper was done. XRD was carried out in 2θ range of 30-95 degree and 2 degrees per minutes scan rate using Cu *Kα* (*α*= 0.15406 nm) radiation in a RIGAKU system.

CHAPTER 4

Results and Discussion

- Micro structural Characterization
- Micro hardness analysis
- EDS line scan analysis
- XRD analysis

4.1. Microstructural characterization

4.1.1. Optical microscope studies

The Cu-Ni multilayered composite formed is analyzed under optical microscope after mounting and subsequent polishing procedure of the cross-section of the sample.

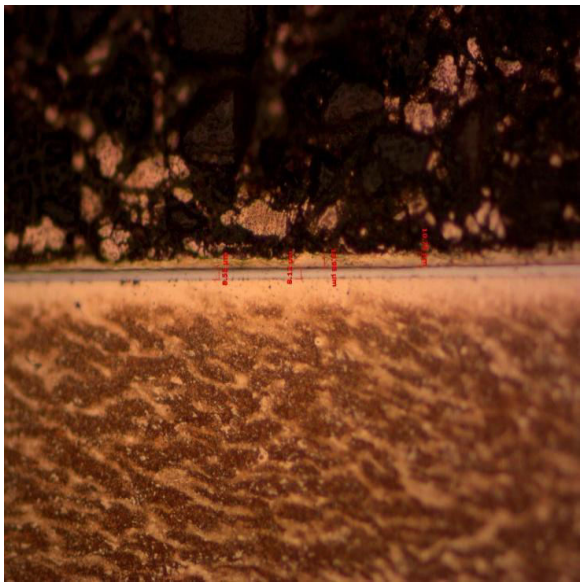


Figure 4.1.Optical micrograph of the cross-section of as electrodeposited Cu-Ni depicting Cu and Ni sub layers thickness 11µm and 8.5µm respectively

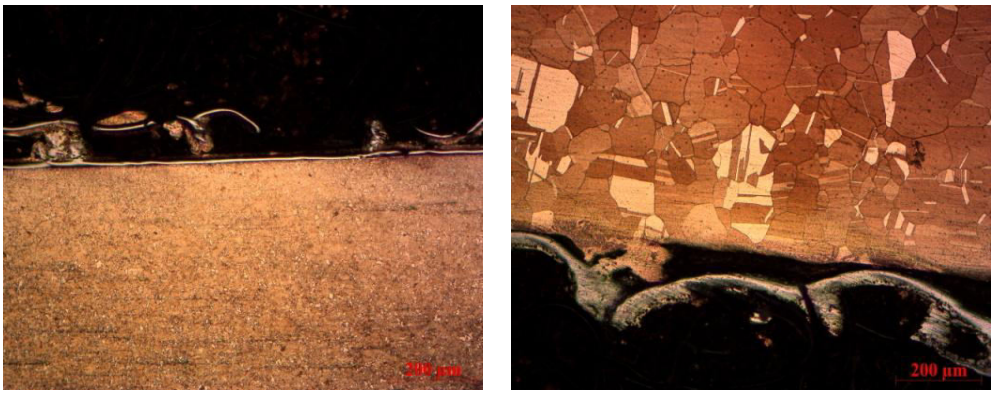
Figure 4.1 depicts the micrograph of the cross-section of an electrodeposited Cu-Ni multilayer composite. For plating time of 20 minutes each for nickel plating and then for copper plating, the analysis shows that the thickness of the nickel layer formed was around 8.5 microns whereas the thickness of the copper layer plated was around 11 microns. Smooth, adherent, continuous and bright layer of nickel had been electroplated.

The Cu-Ni multilayer deposited samples, after heat treatment in the presence of Argon gas at different temperatures (773K, 973K and 1173K) for time periods of 1 hr, 2 hrs and 3 hrs each, were then analyzed under the optical microscope to study the diffusion properties.

Figure 4.2. Optical micrograph of the cross-section of a Cu-Ni multilayer composite, heated at 900^{o}C for 1 hr

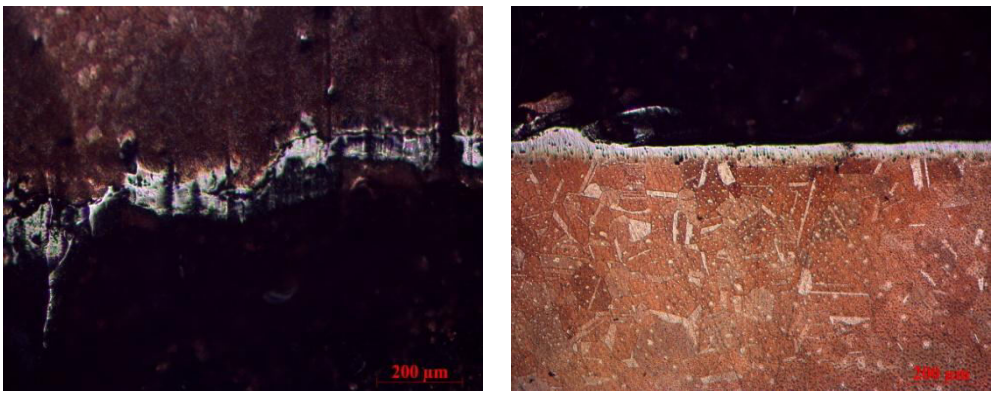
Figure 4.2 depicts the optical micrograph for a Cu-Ni multilayer sample subjected to vacuum annealing in the presence of argon gas at 900^{o}C, for time period of 1 hour. The nickel layer has been displaced slightly due to the high temperature heating involved and subsequent cross section cutting and mounting. But the differentially colored layers of Cu and Ni are visible clearly.

Figure 4.3 (a) shows the optical image of a Cu-Ni multilayer composite, vacuum heated at 500^{o}C for 2 hrs and figure 4.3 (b) depicts the image for a sample heated at 900^{o}C for 2 hrs, with all the electroplating of Cu and Ni layers done with a plating time of 40 minutes. Diffusion at a greater time results in greater diffusion extent for Cu in Ni and Ni in Cu.



(a) (b)

Figure 4.3. (a) Optical micrograph of a Cu-Ni multilayer sample, heated at 500^{o}C for 2 hrs (b) Optical micrograph of a Cu-Ni multilayer sample, heated at 900^{o}C for 2 hrs



(a) (b)

Figure 4.4. (a) Optical micrograph of a Cu-Ni multilayer sample, heated at 700^{o}C for 3 hrs (b) Optical micrograph of a Cu-Ni multilayer sample, heated at 900^{o}C for 3 hrs

Figure 4.4 (a) shows the optical image of a Cu-Ni multilayer composite, vacuum heated at 700^{o}C for 3 hrs and figure 4.4 (b) depicts the image for a sample heated at 900^{o}C for 3 hrs, with all the electroplating of Cu and Ni layers done with a plating time of 40 minutes. Nickel layer having bright and adherent deposits have been formed.

4.1.2. SEM and FESEM analysis

The Cu-Ni multilayered composite formed is analyzed under SEM and FESEM after mounting and subsequent polishing procedure of the cross-section of the sample, for better clarity, magnification and resolution.

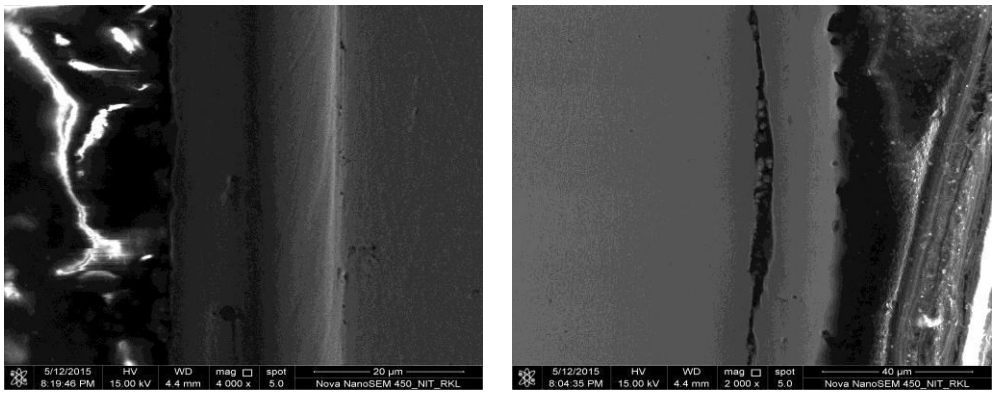


Figure 4.5. (a) FESEM micrograph of a Cu-Ni multilayer sample, heated at 500^{o}C for 2 hrs (b) FESEM micrograph of a Cu-Ni multilayer sample, heated at 900^{o}C for 2 hrs

Figure 4.5 (a) shows the FESEM image of a Cu-Ni multilayer composite, heated in inert atmosphere at 500^{o}C for 2 hrs and figure 4.5 (b) depicts the image for a sample heated at 900^{o}C for 2 hrs, with all the electroplating of Cu and Ni layers done with a plating time of 40 minutes.

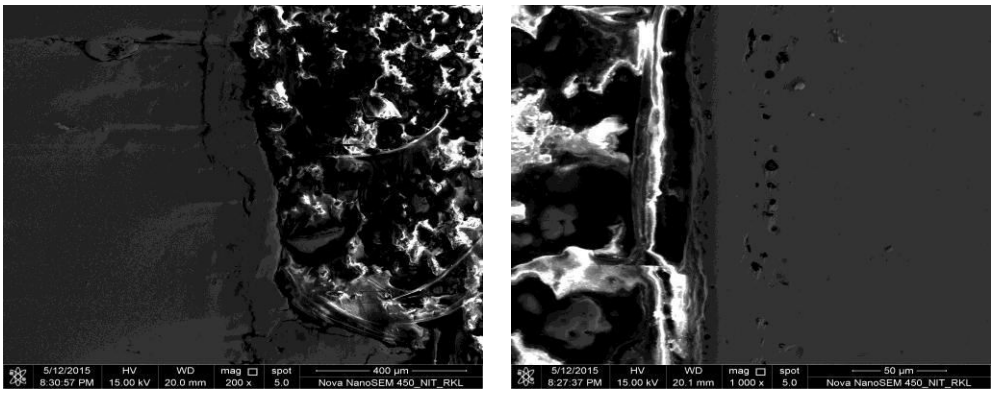


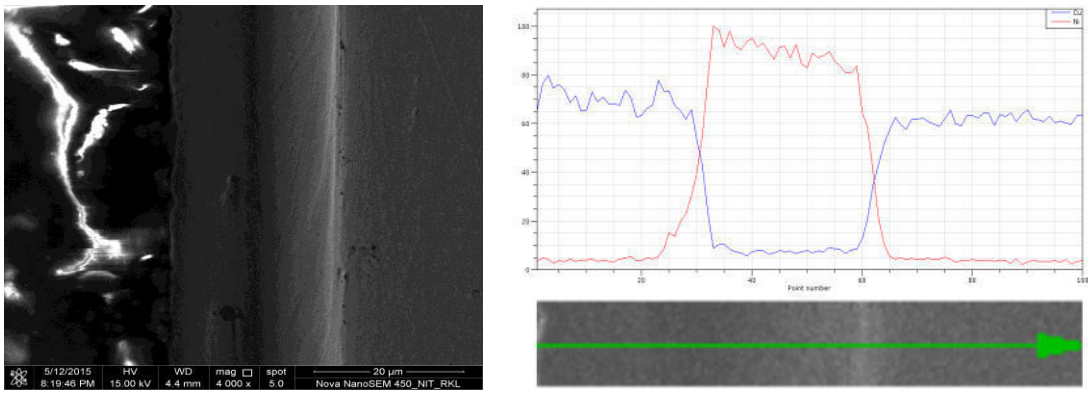
Figure 4.6. (a) FESEM micrograph of a Cu-Ni multilayer sample, heated at 700^{o}C for 3 hrs (b) Optical micrograph of a Cu-Ni multilayer sample, heated at 900^{o}C for 3 hrs

Figure 4.6 (a) shows the optical image of a Cu-Ni multilayer composite, vacuum heated at 700^{o}C for 3 hrs and figure 4.6 (b) depicts the image for a sample heated at 900^{o}C for 3 hrs, with all the electroplating of Cu and Ni layers done with a plating time of 40 minutes.

4.2. Microhardness measurement

The microhardness of the electrodeposited Cu-Ni multilayer was measured to be 142 HV, whereas the hardness values for heated samples showed a decrease in trend, for example, the sample heated at 773K for 2 hrs showed 96 HV hardness and the sample heated at 773K for 1 hr depicted 111 HV hardness. In spite of diffusion and subsequent alloying of Cu and Ni as per the isomorphous Cu-Ni system, the decrease in hardness can be attributed towards release of strain accumulated in electrodeposited layer and recrystallisation/ grain growth during heating.

4.3. EDS line scan analysis



(a) (b)

Figure 4.7. (a) FESEM micrograph of a Cu-Ni multilayer sample, heated at 500^{o}C for 2 hrs (b) EDS line scan of a Cu-Ni sample, heated at 500^{o}C for 2 hrs

Figure 4.7 (a) depicts the FESEM micrograph of a Cu-Ni multilayer sample heated at 500^{o}C for 2 hrs and the diffusion profile for the same Cu-Ni sample is demonstrated by EDS line scan, showing the variation of copper and nickel concentrations with respect to the depth of the sub layers starting from the surface. The blue profile indicates the copper concentration with respect to diffusion depth, showing that the copper concentration is maximum from the surface to the interface of Cu-Ni layers and then gradually decreases to a minimum owing to the diffusion of copper in nickel and then gradually increases to a maximum value again, from the start of the Cu-Ni layer interface.

The red profile indicates that concentration variation of nickel is due to the diffusion of nickel in copper layer. Thus, the Cu-Ni multilayer system forms a diffusion zone with copper and nickel diffusing into each other and hence, the concentration profile variation.

Calculations of diffusion parameters for diffusion of copper in nickel:

Now, from the EDS line scan in figure 4.7 (b), calculating the diffusion distance, x, we get

Diffusion distance, x = 18 µm

for, Temperature of heating, T = 773K

Heating time, t = 2 hrs = 7200 sec

So, $x^2 = 324\ \mu m^2$

Similarly, obtaining the x^2 values, for the other samples heated at 773K for different time intervals t (1 hr, 2 hrs and 3 hrs), from their respective EDS line scans, we have the following table 4.1.

Table 4.1: x^2 (in μm^2) values for heating temperature 773K and time t

Time t ($x10^3$ sec)	x^2 (in μm^2)
3.6	156.25
7.2	324
10.8	529

We know that, for unsteady state diffusion process,

$$\frac{x2}{Dt} = constant$$

Or, $x^2 = Kt$

Where K is a constant for each temperature T and is proportional to D.

Now by plotting the data for x2 versus t, we get the graph shown in figure 4.8.

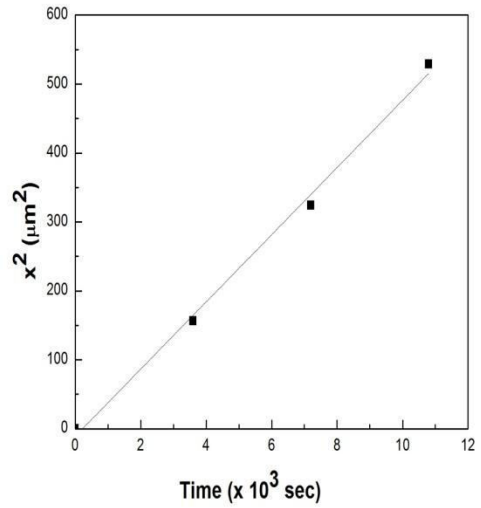


Figure 4.8. x^2 vs t plot for sample heated at 500^{o}C

In figure 4.8, the slope of the graph gives the K value, $K_{773} = 4.5 \text{ X } 10^{-14}$ m^2s^{-1}.

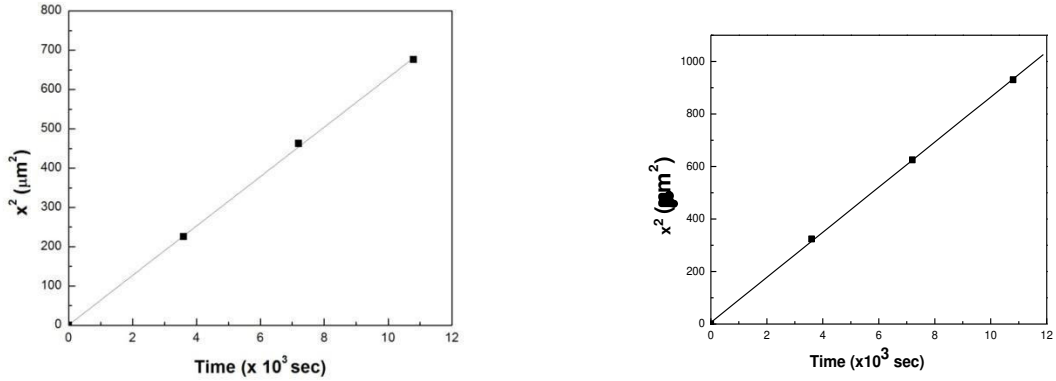
Similarly, table 4.2 and table 4.3 gives the data for x^2 for temperatures of heating 973 K and 1173K for different time periods respectively and the corresponding x^2 vs t plots are shown in figures 4.9(a) and 4.9(b).

Table 4.2: x^2 values for heating temperature 973K

Time t (x10^3 sec)	x^2 (in μm^2)
3.6	225
7.2	462.25
10.8	676

Table 4.3: x^2 values for heating temperature 1173K

Time t ($x10^3$ sec)	x^2 (in μm^2)
3.6	324
7.2	625
10.8	930.25



(a) (b)

Figure 4.9. (a) x^2 vs t plot for sample heated at 700°C

(b) x^2 vs t plot for sample heated at 900°C

The slope of the graphs plotted in figures 4.9(a) and 4.9(b) gives the values for K as, K_{973} = 6.25 x 10^{-14} m^2s^{-1} and K_{1173} = 8.6 x 10^{-14} m^2s^{-1} respectively.

Figure 4.10 depicts the x^2 vs t plots for different temperatures of heating and time periods and clearly illustrates that greater the temperature of heating and time of heating, greater is the diffusion extent or the diffusion depth, i.e.,

$$K_{1173} > K_{973} > K_{773}$$

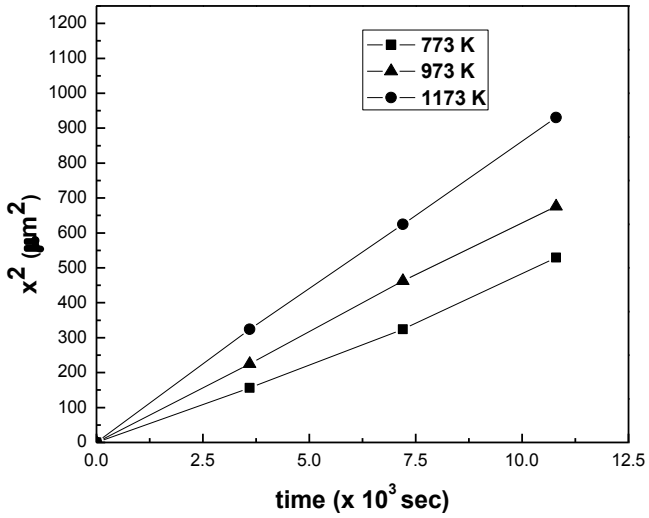


Figure 4.10.x^2 vs t plots for different temperatures of heating and time periods

Now, the K values obtained from the above figures were used to plot a graph between ln K versus 10^4/T so as to obtain the activation energy Q for diffusion of copper in nickel layer. The slope of the graph illustrated in figure 4.11 is equal to Q/R since from the temperature dependence equation for diffusion:

$$\ln K = \ln K_0 - \frac{Q}{RT}$$

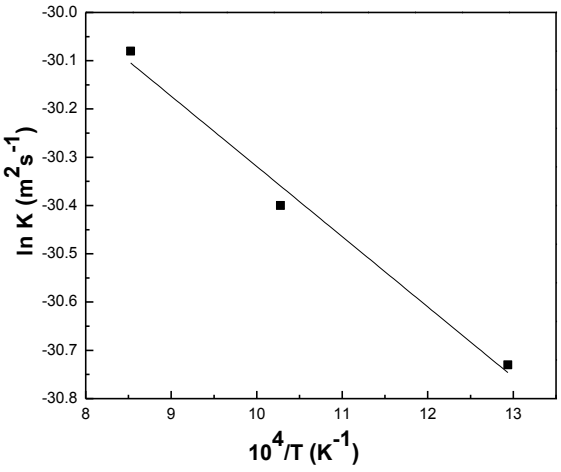


Figure 4.11. lnK vs 1/T plot to obtain the diffusion parameters

The Arrhenius parameters K_0 and Q obtained from the graph as $K_0 = 8.9 \times 10^{-14}$ m^2s^{-1}

and Q = 12.81 kJ/mol-K

The values for diffusion parameters obtained were compared with the standard values for diffusion of copper in nickel and it was seen that the diffusion coefficient obtained for diffusion of copper in nickel was higher than that of the standard value and the activation energy was lower.

4.4. XRD analysis

Since high values for diffusion of copper in nickel were obtained, the structure of Cu-Ni layer was studied. The top layer of Cu was subjected to XRD analysis to check the crystallite size of copper. Figure 4.11 depicts the Cu peaks and it can be observed that the peaks are broad in nature. Formation of fine structure during electrodeposition is a common phenomena and to ascertain this crystallite size was measured from the peak broadening.

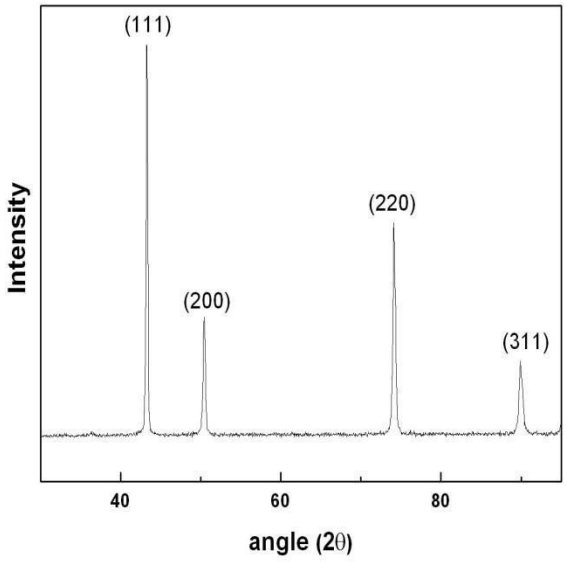


Figure 4.12. XRD analysis for Cu-Ni sample showing peak Broadening

The crystalline size of Cu is calculated using Scherrer formula:

$$D = \frac{0.94\lambda}{\beta cos\theta}$$

Where D is the crystalline size, β is the full width at half maximum (FWHM) of the diffraction peak (111), λ is the wavelength of the incidental X-ray (1.54 A°) and θ is the diffraction angle.

The obtained value for Cu grain size was ~85 nm. In case of Ni layer also similar fine structure can be seen which is quite common and reported earlier.

This extreme fine (nanometric) grain size can play vital role in faster diffusion process by providing more of grain boundary path over bulk diffusion. Apart from this the higher value of diffusion constant can also be attributed towards the accumulated strain of the electrodeposited layers. But after initial heating this effect will fade out slowly due release of the same and recrystallization. Moreover, in the present study inter-diffusion is happening due to similar size of u and Ni atoms. This can help diffusion of a particular species. So, the diffusion of Cu in Ni is actually assisted by diffusion of Ni in Cu and vice versa.

CHAPTER 5

Conclusions

5.1. Conclusions

In this body of work, attempt was made to develop electrodeposited copper-nickel multilayer followed by its diffusion characteristics study. From the detailed investigation conducted, following are the conclusions that can be drawn and established:

1. The copper-nickel multilayer composites were **successfully electrodeposited** with nickel deposited from Watts bath on a copper substrate and subsequent deposition of copper from sulphate bath. The copper and nickel layers electroplated were found to be smooth, adherent and bright with considerable thicknesses which were demonstrated by microstructural study.
2. The electrodeposited copper-nickel samples were then subjected to annealing, in the presence of argon gas, at different temperatures (773K, 973K and 1173K) and time periods (1 hr, 2 hrs and 3 hrs). The microhardness values obtained depicts that hardness decreases with increasing heating temperatures and also with increasing the heating time due to **recrstallization and grain growth** of the initial fine structure.
3. The diffusion parameters for diffusion of copper in nickel were calculated from the EDS line scan analysis of the annealed multilayer samples and when compared with the standard data, discrepancy was found. The observed values of copper diffusion in nickel were found to be greater than the standard values and this increase was attributed to the following factors:
    I. The crystalline size of copper was determined to ~be 85 nm from the XRD analysis and thus, this **fine crystalline size** results in greater grain boundary diffusion.

II. Since only the diffusion of copper in nickel was considered during the determination of diffusion parameters, so the increase can be due to the fact that nickel also diffuses in copper to a considerable extent and this **interdiffusion** of copper in nickel and nickel in copper at the Cu-Ni layer interface leads to the increase in the diffusion rate due to easy availability of vacancies.

III. **Internal strain** in the multilayers could also be taken as a deciding parameter for the diffusion extent at least at the initial period of the annealing.

CHAPTER 6

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